A-20303/A/CONT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF

FRANCOIS GUGUMUS

SERIAL NO. 08/858,191

FILED: April 21, 1997

FOR: SYNERGISTIC STABILIZER MIXTURE

Group Art Unit: 1511

Examiner: V. Hoke

Commissioner of Patents and Trademarks

Washington, D.C. 20231

DECLARATION UNDER 37 CFR 1.132

I, François Gugumus, a citizen of France and a resident of 4123 Allschwil, Switzerland, hereby declare:

That I was awarded the degree of a Doctor of Science by the University of Strassbourg, France, in 1965.

That I have been employed by Ciba-Geigy AG, now Ciba Specialty Chemicals Inc., as Chemist in the Additives Division and have been engaged in the field of stabilizers for polymers since 1970.

That I am an inventor of numerous U.S. Patents, for example Nos. 4,148,783; 4,692,486; 4,623,480 and 4,734,449 assigned to Ciba-Geigy Corp.

That I am the author of numerous technical articles relating to the same or closely related field of research, for example:

"Progrès dans la protection des materières plastiques contre le rayonnement UV", Kunststoffe-Plastics 22 (1975), 11-19;

"Developments in the UV stabilization of polymers", Developments in Polymer Stabilization, Applied Science Publishers Ltd., London, 1979, 261-308;

"Contribution to polyethylene photooxidation", Angewandte Makromolekulare Chemie 158/159 (1988), 151-176;

"Antioxidantien", Kunststoffe 77 (1987), 1070-1107;

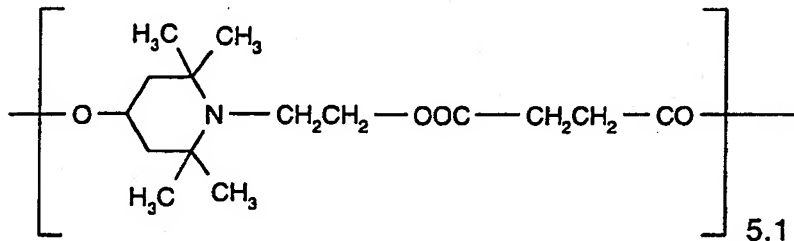"Lichtschutzmittel", Kunststoffe 77 (1987), 1165-1210;

"The use of accelerated tests in the evaluation of antioxidants and light stabilizers", Developments in Polymer Stabilization, Applied Science Publishers Ltd., London, 1987, 239-289.

That I am the inventor of U.S. Patent Application Serial No. 08/858,191.

That the experiments described in the following have been made under my supervision and the evaluation of the results has been done by myself.
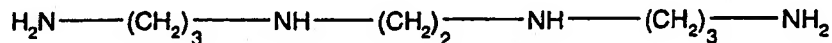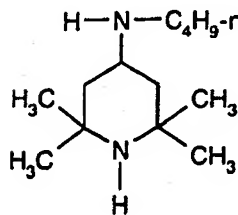
STABILIZERS TESTED:

Compound A:

$$\left[O - \underset{\underset{H_3C \quad CH_3}{}}{\overset{\overset{H_3C \quad CH_3}{}}{\bigcirc}} N - CH_2CH_2 - OOC - CH_2CH_2 - CO \right]_{5.1}$$

Compound B:

A product obtainable by reacting an intermediate product, obtained by reaction of a polyamine of the formula

$$H_2N - (CH_2)_3 - NH - (CH_2)_2 - NH - (CH_2)_3 - NH_2$$

with cyanuric chloride, with a compound of the formula

$$H - N - C_4H_9\text{-}n$$

$$\underset{\underset{H}{N}}{\overset{\overset{H_3C \quad CH_3}{}}{\bigcirc}} \quad \underset{H_3C \quad CH_3}{}$$

TEST METHOD A:

100 parts of polypropylene powder (melt flow index: ~ 2 g/10 min at 230°C and 2160 g) are blended in a barrel mixer with 0.05 parts of pentaerythrityl-tetrakis{3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate}, 0.05 parts of tris{2,4-di-tert-butylphenyl} phosphite, 0.1 parts of Ca stearate and the amount of stabilizer indicated in Table 1. Then, the blend is compounded in an extruder at temperatures of 180 - 220°C. The granules obtained on extrusion and granulation are transformed into films at 220 - 260°C in a second extruder equipped with a flat sheet die. The films are cut into ribbons which are drawn to achieve a stretch ratio of 1:5. The tapes obtained with this procedure are finally 50 μm thick and 2.5 mm wide.

The tapes are mounted without tension on sample holders and exposed in a WEATHER-OMETER Ci 65 (black panel temperature 63 $\pm$ 2°C, without water-spraying). Periodically, the tensile strength of the exposed tapes is measured. The exposure time (T_{50}) corresponding to a loss of 50 % of the initial tensile strength is a measure for the efficiency of the stabilizer.

A synergistic effect of a stabilizer mixture is determined by a comparison of a calculated T_{50} value with the actually measured T_{50} value. The T_{50} values are calculated on the basis of the additivity law (B. Ranby and J.F. Rabek; Photodegradation, Photo-oxidation and Photostabilization of Polymers, Principles and Applications, John Wiley & Sons, London, New York, Sydney, Toronto, 1975, pages 418 and 419) according to the following equations, when, in the polypropylene, the overall concentration of the stabilizer is 0.1 %:

("%" means always "% by weight, relative to the weight of the polypropylene")

Expected stabilizing activity for a mixture of 0.025% (A) and 0.075% (B)
= 0.25 {Stabilizing activity of 0.1% (A), alone} + 0.75 {stabilizing activity of 0.1% (B), alone}

Expected stabilizing activity for a mixture of 0.033% (A) and 0.066% (B)
= 0.33 {Stabilizing activity of 0.1% (A), alone} + 0.66 {stabilizing activity of 0.1% (B), alone}

Expected stabilizing activity for a mixture of 0.05% (A) and 0.05% (B)
= 0.5 {Stabilizing activity of 0.1% (A), alone} + 0.5 {stabilizing activity of 0.1% (B), alone}

Expected stabilizing activity for a mixture of 0.066% (A) and 0.033% (B)
= 0.66 {Stabilizing activity of 0.1% (A), alone} + 0.33 {stabilizing activity of 0.1% (B), alone}

Expected stabilizing activity for a mixture of 0.075% (A) and 0.025% (B)
= 0.75 {Stabilizing activity of 0.1% (A), alone} + 0.25 {stabilizing activity of 0.1% (B), alone}

Since, in the indicated concentration range, the stabilizing activity of the single stabilizers linearly increases with the concentration, the same overall concentration of the stabilizers (0.1%) has to be used for the calculation of the activity expected from a stabilizer mixture.

The values obtained are summarized in Table 1.

The stabilizer mixture shows a synergistic effect, when $T_{50\,measured} > T_{50\,calculated}$.

<u>Table 1:</u>

Stabilizer	(A)/(B) ratio	$T_{50\,measured}$ / hours [*]	$T_{50\,calculated}$ / hours
Control	——	685	——
0.1 % (A)	——	3100	——
0.1 % (B)	——	4400	——
0.025 % (A) and 0.075 % (B)	1:3	4200	4075
0.033 % (A) and 0.066 % (B)	1:2	4650	3930
0.05 % (A) and 0.05 % (B)	1:1	4650	3750
0.066 % (A) and 0.033 % (B)	2:1	4000	3500
0.075 % (A) and 0.025 % (B)	3:1	3700	3425

[*] High values indicate a good stabilizing activity

The data shown in Table 1 clearly reveal a synergistic effect.

TEST METHOD B:

100 parts of polypropylene powder (melt flow index ~ 3.5 g/10 min at 230°C and 2160 g) are blended in a barrel mixer with 0.05 parts of pentaerythrityl tetrakis{3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate}, 0.05 parts of tris{2,4-di-tert-butylphenyl} phosphite, 0.1 parts of Ca stearate and the amount of stabilizer indicated in Figures I and II. Then the blend is compounded in an extruder at temperatures of 180 - 220°C. The granules obtained on extrusion and granulation are transformed into films at 220-260°C in a second extruder equipped with a flat sheet die. The films are cut into ribbons which are drawn to achieve a stretch ratio of 1:6. The tapes obtained with this procedure are finally 50 μm thick and 2.5 mm wide.

The tapes are mounted without tension on sample holders and subjected to natural weathering in Florida (45° South, direct, approximately 140 kLy/year).
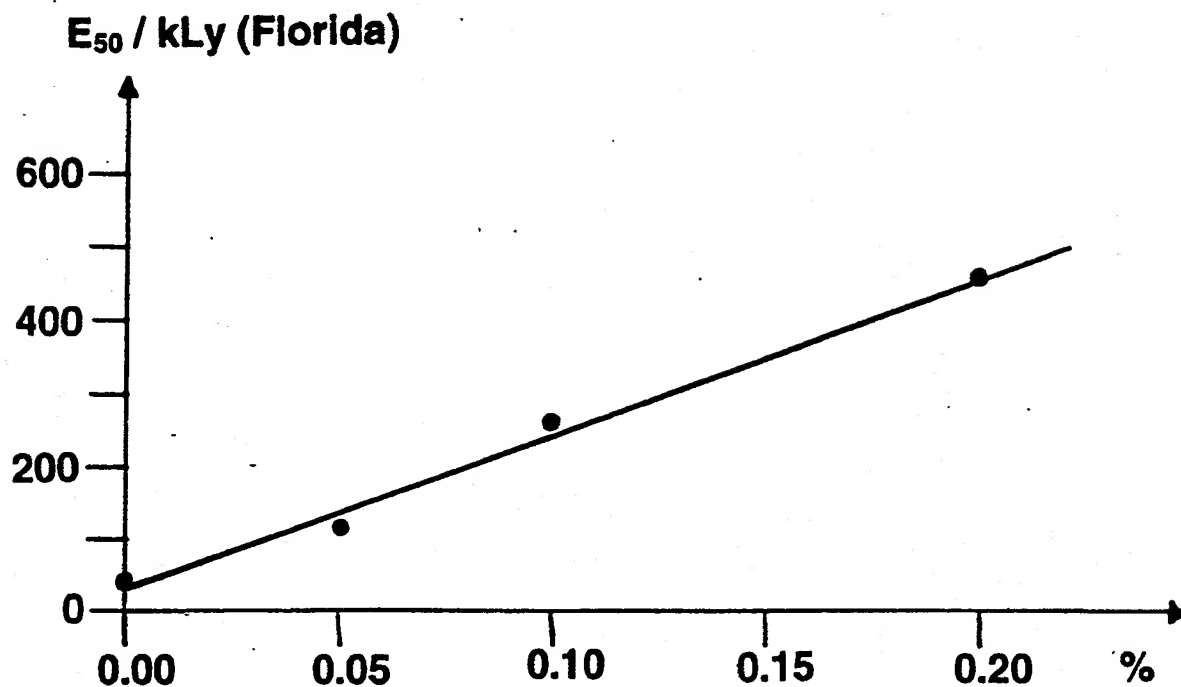Periodically , the tensile strength of the exposed tapes is measured.The received energy (in kLy) corresponding to a loss of 50 % of the initial tensile strength (E_{50}) is a measure for the stabilizing efficiency of the light stabilizer.

The values obtained are shown in Figures I and II which clearly reveal that, in the indicated range, the activity of the stabilizers tested <u>linearly</u> increases with the concentration.

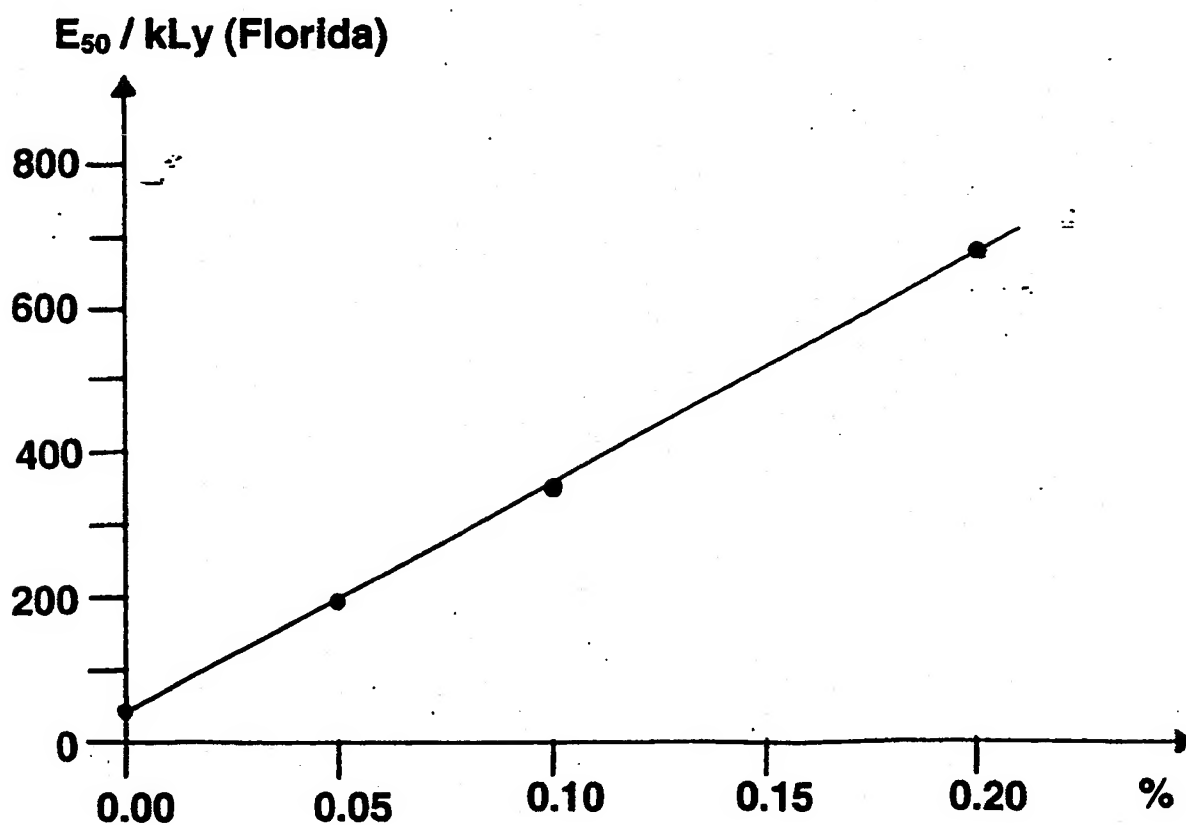"%" means "% by weight of the stabilizer, relative to the weight of the polypropylene")

Concentration dependency of the stabilizing activity of (A)

E$_{50}$ / kLy (Florida)

Concentration dependency of the stabilizing activity of (B)

E$_{50}$ / kLy (Florida)

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this _6th_ day of _April 1998_

François Gugumus

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